The magnetite-maghemite-hematite transformation

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Magnetite (Fe_3O_4), which is ubiquitous in the crust, is transformed into hematite (α-Fe_2O_3) by the oxidation of Fe^{2+} to Fe^{3+}. In this oxidation process, maghemite (γ-Fe_2O_3) is formed as an intermediate phase, which is isomorphous as magnetite. Maghemite has a part of the octahedral site in magnetite that is vacancy. Elucidation of the oxidation mechanism of magnetite will lead to elucidation of magnetic susceptibility changes during weathering of igneous and sedimentary rocks, but continuous changes in local structure of magnetite are largely unknown. In this study, in order to elucidate the mechanism of the phase transition from magnetite to hematite via maghemite, X-ray absorption fine structure (XAFS) and X-ray diffraction (XRD) measurements were used to determine the area around Fe in the oxidation process of magnetite. We investigated the continuous local structural change of, and the change of long-range structure of the whole crystal.
XANES showed that the proportion of Fe^{3+} increased with increasing heating temperature and heating time, and finally all Fe became Fe^{3+}. From the radial structure function of EXAFS, it was found that the peak depending on the presence of Feoct in magnetite attenuated as the heating temperature increased, and then changed to a function indicating the structure of hematite. From the XRD, as the heating temperature increases and the heating time increases, first, octahedral vacancies have characteristic peaks in ordered maghemite, and then magnetite and maghemite peaks decrease, and hematite peaks appear and increase. From the above results, in the oxidation of magnetite, the Fe-O bond of some octahedral site is broken first, and Fe diffuses to become maghemite. Then, the rearrangement of Fe and O in the octahedral site with a vacancy at the center and the Fe-O4 tetrahedral site is thought to cause a phase transition to a hematite consisting entirely of octahedra.

Keywords: Magnetite, Maghemite, Hematite, XRD, XAFS

